MISSOURI DEPARTMENT OF NATURAL RESOURCES
DIVISION OF ENVIRONMENTAL QUALITY
ENVIRONMENTAL SERVICES PROGRAM
Standard Operating Procedures

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SOP TITLE: Sampling Water and Other Liquids for Volatile Organic Analysis (VOA)

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SUMMARY OF REVISIONS: Procedures under section 7.1 on Surface Water Samples were revised to include specific collection methods for filling sample vials. Section 8.0 on Handling and Preservation was revised to include the preservation methodology for collection of a VOC sample from a chlorinated drinking water source. Minor grammatical and style revisions were also made throughout the entire document.

APPLICABILITY: The procedures described in this SOP are applicable to all ESP personnel who collect water or other liquid samples for VOA.

DISTRIBUTION: Regional Directors: JCRO, SLRO, KCRO, NERO, SERO, SWRO
Program Directors: ESP, HWP, WPCP, SWMP
ESP Supervisors: FSS, EERS
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RECERTIFICATION RECORD:

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1.0 SCOPE AND APPLICABILITY

1.1 This SOP describes the sampling methodology to be followed by ESP personnel when collecting water or other liquid samples for VOA. This includes any type of water sample - surface water, groundwater, wastewater, potable water - and any other type of liquid sample, including liquid samples of hazardous waste. These procedures were previously described in MDNR-FSS-006 *Sample Collection For Volatile Organic Analysis (VOA).* However, MDNR-FSS-006 included sample collection procedures for both liquid and solid media. Because the methodology prescribed for the collection of liquid vs. solid media is so different, it was decided to develop two separate SOPs to cover these two sets of procedures. Refer to MDNR-FSS-006B *Sampling Soils and Other Solid Media for Volatile Organic Analysis (VOA)* for guidance in collecting soil, sludge or other solid media for VOA.

2.0 SUMMARY OF METHOD

2.1 Volatile organic compounds are the most sensitive group of chemicals that are routinely analyzed in environmental investigations. Aeration, agitation, heat, pressure changes, and microbial degradation reduce the amount of volatiles in a sample and can result in data that are negatively biased. Loss of volatiles through sampling techniques and microbial degradation is reduced through the use of minimal disturbance, no headspace, and proper preservation. This SOP describes the methodology that should be followed when collecting water and other liquid samples for VOA. Procedures for preservation techniques, sample handling, and transportation are also covered. By following the methods described in this SOP, sampling personnel will be able to collect volatile organic samples that will be representative of the media sampled.

3.0 DEFINITIONS AND ACRONYMS

- HASP - Health and Safety Plan
- OSHA - U.S. Occupational Safety and Health Administration
- PID - Photoionization Detector - Portable air monitoring instrument used to measure the amount of ionizable organic vapors present
- Volatile Organics – Organic compounds that have a boiling point less than 200 °C

4.0 HEALTH AND SAFETY REQUIREMENTS

4.1 Sampling personnel need to be aware of the hazards of working with concentrated hydrochloric acid (HCl), the preservative used when collecting water samples for volatile organics analysis. Although, the quantity of acid in each pre-preserved sample vial is small (3-4 drops per vial), there still exists a splash hazard when collecting and handling VOA samples. All sampling personnel should wear safety glasses when collecting volatile organic samples in a pre-preserved sample container. Material Safety Data Sheets are available to all ESP personnel who desire further information on HCl.

4.2 For sampling investigations that occur at hazardous waste sites, more detailed health and safety requirements will be described in site specific HASPs. Personnel who conduct work at hazardous waste sites will be expected to read and comply with the requirements of any site specific HASP.

4.3 All ESP personnel who conduct work at hazardous waste sites will be required to participate in the DEQ's medical monitoring program.

5.0 PERSONNEL QUALIFICATIONS

5.1 Hazardous Waste Operations and Emergency Response (HAZWOPER) Site Work

5.1.1 All ESP personnel directly involved in field investigations at sites that fall under the EPA Worker Protection requirements of 40 CFR Part 311, referencing OSHA 29 CFR Part 1910.120, and meet the definition of HAZWOPER activities must meet the following qualifications:

5.1.1.1 Attend a 40-hour course designed to meet the OSHA health and safety training requirements for hazardous site workers;

5.1.1.2 Attend an annual 8-hour health and safety refresher course, or receive equivalent training;

5.1.1.3 Participate in a medical monitoring program;

5.1.1.4 Receive appropriate on-the-job training;

5.1.1.5 Be familiar with the *Hazardous Substance Emergency Response Plan*, written and maintained by the ESP;

5.1.1.6 Be familiar with the ESP SOP manual and have read all SOP documents that are applicable to the field activities, including but not limited to those referenced in this SOP.

5.2 Non-Hazardous Site Work

5.2.1 All ESP personnel who conduct field or sampling investigations at sites that do not fall under HAZWOPER regulations (e.g., stream surveys), must meet the following qualifications:

5.2.1.1 Receive appropriate on-the-job training;

5.2.2.2 Be familiar with the ESP SOP manual and have read all SOP documents that are applicable to the field activities, including but not limited to those referenced in this SOP.

6.0 SUPPLIES AND EQUIPMENT

6.1 At a minimum, the following supplies and equipment will be needed to properly collect, preserve, and handle water or other liquid samples for VOA:

- 40-60 ml purgable glass vials with Teflon-coated septa (pre-preserved for aqueous samples)
- 1.5 oz. or larger glass containers with Teflon lid liners (unpreserved for non-aqueous samples)
- nitrile gloves
- plastic ziplock bags
- cooler with ice
- sample labels (both pre-numbered and blank)
- Field Sheet and Chain-of-Custody Record forms
- field notebook
- trip blank
- level D personal protective equipment

6.2 Other equipment and supplies may also be needed depending upon special requirements that may be specified in a sampling plan and/or a HASP, the type of media sampled (e.g., groundwater), or other site-specific circumstances. The following list is not intended to be all-inclusive but merely suggests many common optional supplies and equipment that may be helpful when conducting a field investigation that involves the collection of water or other liquid samples for VOA:

- PID
- clean, graduated 5-gallon bucket
- oil-water interface probe
- pH meter
- conductivity meter
- camera
- level B or C personal protective equipment
- bottle of analyte-free water for the collection of rinsate blanks and/or field blanks

7.0 PROCEDURE

7.1 Surface water samples

7.1.1 Two, certified clean, 40-60 ml purgable glass vials with Teflon-coated septa must be filled for each sample. Refer to MDNR-FSS-001 *Containers, Volumes, Preservatives, Holding Times, and Special Considerations* for more information.

7.1.2 Sample vials should be pre-preserved with HCl. If pre-preserved vials are not available in the field, then a valid sample can still be obtained using unpreserved sample vials. However, samples that are not chemically preserved have a shorter holding time (7 days vs. 14 days for a preserved sample). If sample vials were not pre-preserved and HCl was not available at the moment of collection, the vials should not be opened after collection just to add preservative. Opening the vials at a later time to add preservative will result in a loss of volatiles. In the event that unpreserved samples are returned to the lab, the sample custodian must be notified about the discrepancy. The results for an unpreserved sample will still be valid if the analysis is performed within the holding time for an unpreserved sample.

7.1.3 Each sample vial for volatile organics analysis must be completely filled with no headspace remaining in the vial. Each vial should be slowly filled by submerging the vial directly into the body of water being sampled. Unless the sample collector specifically wants to collect a material floating on the surface of the water, such as a layer of petroleum contamination, any scum or other floating debris on the water should be brushed away with a clean gloved hand prior to sample collection. The decision whether or not to collect a visible floating layer of petroleum contaminant or other light non-aqueous phase liquid (LNAPL) is dependant upon the purpose of the sampling. If only the water soluble, or dissolved, phase of the contaminant is desired, then the floating layer or LNAPL should be brushed away and avoided if possible. If a sample of the more concentrated, separate phase of the LNAPL is desired, then no efforts should be made to brush away the LNAPL and it should be collected as part of the water sample. The vial should be held right side up and tilted at a slight angle with the open rim positioned at the water's surface. Each vial should be filled slowly, not only to reduce the amount of agitation and aeration of the sample but also to avoid overfilling the vial since the vial should be pre-preserved with a small amount of HCl and overfilling could inadvertently flush out or over-dilute the acid.

7.1.4 Sometimes, because of accessibility problems or safety concerns, direct submersion of sample vials is not feasible. In that case, the use of a sampling device, such as a dipper, may be necessary. A discussion of the many different types of water sampling devices that may be used is beyond the scope of this SOP. However, it should be mentioned that when a sampling device is used to collect a water sample for volatile organics, care should be taken to eliminate or reduce as much as possible any agitation or aeration of the sample as it is being collected and transferred to the sample vials. The sample collector should select a sampling device that is clean and constructed out of materials that are chemically compatible with the sample media and the volatile organic parameters of interest.

7.1.5 Each sample vial must be filled to the point that there is a convex meniscus on the top of the vial. The vial must then be securely capped. The vial should be inverted and gently tapped against the hand as the sample collector observes the vial looking closely for any air bubbles that may be present. If there are any visible air bubbles, the sample should be discarded and another vial should be used for sample collection. Reopening the vial and topping it off can result in a loss of volatiles.

7.1.6 Once the vials have been filled and proper labels have been attached, each sample (two vials per sample) should be placed into a ziplock bag. The ziplock bag acts as a secondary container and helps keep the sample vials relatively dry when stored on ice. The sample vials should then be placed in a cooler on ice. Refer to MDNR-FSS-003 *Sample Numbering and Tagging* for procedures on using sample labels.

7.1.7 When collecting a water sample from a lake, stream, or other surface water body, care should be taken to avoid stirring up sediment and incorporating that sediment into the sample. Refer to MDNR-FSS-005 *General Sampling Considerations Including the*

Collection of Grab, Composite, and Modified Composite Samples from Streams and Wastewater Flows for further guidance on collecting surface water samples.

7.2 Potable water samples

7.2.1 Potable water samples are usually collected from a tap or spigot at a residential or business location. The procedures described above for 7.1.1 through 7.1.5 are general procedures that are common to the collection of all water samples for volatile organic parameters and should be followed for sampling potable water supplies. There is an exception to the general procedures regarding preservation methodology whenever a potable water sample is collected from a chlorinated drinking water supply and the by-products of chlorination are among the parameters of interest. Refer to section 8.0 for specific preservation methodology for the collection of chlorinated drinking water samples.

7.2.2 The first thing that should be considered is the sampling objective. Most often, a potable water supply is sampled to determine if the source (i.e., the well) is contaminated. On occasion, the objective is to determine if there is contamination in the delivery system and not the well. The sampling objective helps to determine the sampling technique.

7.2.3 When the objective is to determine whether or not the well is contaminated, then the sample should be collected from a tap located as close as possible to the wellhead. If there is a well house, there is usually a tap located there that is suitable for sample collection. If there is no well house, the pressure tank should be located. If there is a tap located between the well and the pressure tank, then a sample should be collected from there. As a last resort, if there are no taps located between the well and the pressure tank, then most any tap will suffice.

7.2.4 When collecting a sample of potable water, the sample must always be collected from a cold water tap.

7.2.5 Once a suitable tap has been selected, the system should be flushed or purged of stagnant water. An estimate should be made of the volume of water in the system, including the capacity of the pressure tank. If well characteristics are known, the volume of water in the well casing should be taken into account. The tap should be opened up at the point where the sample will be collected and the system should be flushed. The discharge rate should be measured using a 5-gallon bucket, or other large container of known size, and a stopwatch. The total volume purged should be recorded in a field notebook.

7.2.6 Once the system has been adequately purged of stagnant water, the tap should be turned down to where the flow is a slow trickle. The key to collecting a representative sample is minimal disturbance. The sample vial should be tilted so that the water flows down the side and doesn't splash on the bottom of the container. The steps described in 7.1.1 through 7.1.5 should be followed.

7.2.7 When the objective is to determine whether contamination exists in the system and not the well, then flushing should not be done. The sample should be collected from a tap within the distribution system beyond or downstream of the point where contaminants may be suspected of entering the system. The sample should be collected without flushing or purging and should be done following the same procedure outlined in step 7.2.6.

7.3 Monitoring well samples

7.3.1 Bailers

7.3.1.1 Disposable, single-use bailers are best since they eliminate the need for decontamination and eliminate the potential for cross-contamination when using a bailer in more than one well. Bailers that are not single-use disposable should be periodically checked for cleanliness through analysis of a rinsate blank to ensure the decontamination procedure being used has been effective.

7.3.1.2 The key to collecting a representative sample is minimal disturbance. Bailers should be lowered slowly into wells to prevent forceful contact with the water table and minimizing disturbance.

7.3.1.3 A small-diameter bottom-emptying device (~ 2 mm diameter) is helpful in slowly transferring the water sample from a bailer to the sample vials. If a small diameter bottom-emptying device is not available, then the water should be slowly poured from the top of the bailer into the sample vials. When pouring from the top, sample contact with the delivery rope or line should be avoided.

7.3.1.4 Groundwater samples should always be transferred directly from the bailer to the sample vials without using any type of intermediate container such as a bucket or other holding or mixing device.

7.3.1.5 The procedures described above for 7.1.1 through 7.1.5 are general procedures that are common to the collection of all water samples for VOA and should be followed for sampling monitoring wells. For more information on sampling procedures for monitoring wells, refer to MDNR-FSS-007 *Collection of Samples From Wells.*

7.3.2 Pumps

7.3.2.1 A discussion of the various types of pumps available for use in monitoring well evacuation and sampling is beyond the scope of this SOP. However when using any pump, there is one procedure that is common to collection of groundwater samples for VOA: when collecting a sample, the flow of the pump should be decreased as much as possible to minimize the amount of agitation and aeration of the sample. The flow should be reduced as far as possible while maintaining a steady flow during sample collection. Refer to MDNR-FSS-007 *Collection of*

Samples From Wells for additional procedures to follow when using pumps for groundwater sampling.

7.3.2.2 The procedures described above for 7.1.1 through 7.1.5 are general procedures that are common to the collection of all water samples for volatile organic parameters and should be followed for sampling monitoring wells using pumps.

7.4 Hazardous waste liquids and other non-aqueous liquid samples

7.4.1 Hazardous waste liquids and other non-aqueous liquid samples collected for VOA should not be collected in pre-preserved vials and should not receive any chemical preservative. Chemical preservatives are unnecessary for samples of concentrated wastes and may cause a severe chemical reaction if added to concentrated waste samples.

7.4.2 Certified clean, glass sample containers with Teflon-lined lids should be used for the collection of hazardous waste liquid and other non-aqueous liquid samples. The sample containers should be 1.5 ounce size or larger.

7.4.2 Hazardous waste liquids and other non-aqueous liquid samples are often collected from drums or tanks. Refer to MDNR-FSS-008 *Collection of Samples From Drums* and MDNR-FSS-009 *Collection of Samples From Tanks* for specific sampling procedures to follow for container sampling.

7.4.3 Zero headspace is not an issue when collecting hazardous waste liquids and other non-aqueous liquid samples. However, provided there is enough material available, each container should be filled as full as practical.

7.4.4 Using paper towels, any gross contamination that may exist on the outside of the sample containers should be wiped off. Each sample container must have a label with pertinent information that is legible. If any visible contamination remains on the outside of the sample container, it should be put in a protective plastic bag before it is placed in a cooler on ice.

7.4.5 If water samples and concentrated waste samples are both collected on the same trip, the waste samples should be placed in one cooler and the water samples in another to minimize the potential for cross contamination during storage and transportation.

7.5 General Considerations

7.5.1 Regardless of the type of media sampled, samples should be collected in the order of least contaminated to most contaminated. This is especially important if any of the sampling equipment is non-dedicated and will be reused while at the site.

7.5.2 A field notebook should be used to record pertinent information when conducting any type of field investigation. MDNR-FSS-004 *Field Documentation* provides guidance for recording permanent notes during a field investigation.

7.5.3 In addition to using a field notebook for documentation, all samples that are returned to the ESP laboratory for analysis or evidentiary purposes must be recorded on a Field Sheet and Chain-of-Custody Record. MDNR-FSS-002 *Field Sheet and Chain-of-Custody Record* provides guidance in using this important documentation record.

8.0 HANDLING AND PRESERVATION

8.1 Except for some chlorinated drinking water samples (i.e. generally those samples collected for public drinking water regulatory concerns), all water samples (surface water, groundwater, potable water, and wastewater) should be collected in 40-60 ml purgable glass vials that have been pre-preserved with HCl. Where there is a concern regarding the by-products of chlorination in a drinking water sample, a two-step preservation process has been developed. The two-step process is discussed below in section 8.2. If chlorination by-products are not of concern, then the two-step preservation process is not necessary. All samples of non-aqueous liquid waste (e.g. oils or suspected hazardous wastes) should not be chemically preserved due to the potential for a severe chemical reaction.

8.2 If the by-products of chlorination are among the volatile organic parameters of interest, then water samples collected from a chlorinated drinking water source must be preserved using a two-step preservation procedure involving sodium thiosulfate and HCl. The sodium thiosulfate is used in the first step to quench or neutralize the chlorine. Sodium thiosulfate crystals are typically added to a sample vial as a pre-preservative. After the water sample has been collected in the vial with the sodium thiosulfate, the vial must be capped and GENTLY inverted a couple of times to dissolve the preservative crystals. There should be no headspace in the vial. The vials should NOT be shaken, since shaking or other severe agitation could release volatile organics from the sample. Once the crystals have dissolved, which should take less than one minute, the vial should be upcapped with the entire contents then poured into another vial that has been pre-preserved with HCl. There should be no headspace in the second, or final vial. The first, empty vial can then be discarded. This procedure must be done with two sets of vials since the sample volumes needed for the two-step procedure are the same as for other water samples collected for volatile organic parameters - two full vials are needed for analysis. This two-step procedure is generally followed only by staff who are collecting samples for the Public Drinking Water Program.

8.3 Immediately upon collection, all samples should be chilled to approximately 4 °C. This is typically accomplished by placing the samples on ice in a cooler. If it is necessary to keep the samples on ice for extended periods of time, the coolers should be periodically drained to ensure that the samples do not become submerged in water from melted ice. Placing the sample containers in ziplock bags also helps to keep the outside of the containers relatively dry.

8.4 When collecting for volatile organic parameters cross-contamination is a concern when aqueous and non-aqueous samples are both collected during the same field investigation. Separate coolers should be used to segregate aqueous samples from non-aqueous samples to minimize the potential for cross-contamination while in storage and transport. One trip blank should be placed in each cooler that holds samples. If there aren't enough trip blank samples to place in each cooler, then the cooler(s) that hold the aqueous samples should be the highest priority and thus should also contain the trip blank samples. For the trip blank samples, the Field Sheet and Chain-of Custody

Record should note with which type of samples (aqueous or non-aqueous) that each trip blank was associated while in transport.

8.5 Caution should be used when collecting, storing, and transporting sample containers when outside ambient temperatures are below freezing to ensure that the samples do not freeze. Since water samples are collected with zero headspace, there is no room for expansion and the containers will break upon freezing.

8.6 For more guidance on sample handling procedures refer to MDNR-FSS-018 *Sample Handling: Field Handling, Transportation, and Delivery to the ESP Lab.*

9.0 QUALITY ASSURANCE/QUALITY CONTROL

The type and frequency of field QA/QC samples needed at any given site are generally covered by Quality Assurance Project Plans. The different types of field QA/QC samples are listed below, with general recommendations on when they may be appropriate. Refer also to MDNR-FSS-210 *Quality Assurance/Quality Control for Environmental Data Collection* for further guidance and information on QA/QC sampling procedures.

9.1 Trip Blank

9.1.1 A minimum of one trip blank sample should be taken to the field by sampling personnel when the collection of water samples for VOA is anticipated.

9.1.2 A trip blank should consist of analyte-free water obtained from the Volatiles Lab within the ESP and preserved with HCl. A trip blank sample is never opened in the field. If the water for a trip blank is obtained from a source other than the Volatiles Lab at the ESP, then it should be recorded in the field notebook.

9.1.3 A trip blank should be packed with the sample containers that will be used during the trip. Once samples have been collected and placed on ice in a cooler, the trip blank should also be put in the cooler. If more than one cooler is used for sample storage, a trip blank sample should be placed in each cooler.

9.2 Field Blank

9.2.1 A field blank is a sample of analyte-free water that is filled while in the field to help determine if there are any air contaminants, such as dust or volatile organic emissions, that may affect a water sample as it is collected. Collection of field blanks is not very common and done only on a site-specific basis.

9.3 Rinsate Blank

9.3.1 A rinsate blank should be collected any time non-dedicated sampling equipment is used to obtain more than one water sample for volatile organics. Non-dedicated sampling equipment requires decontamination between samples and must be periodically tested to

ensure that the equipment is not contributing to cross contamination. Equipment such as pumps and non-disposable bailers used for the collection of groundwater samples fall into this category.

9.3.2 If non-dedicated sampling equipment is used in the field, a minimum of one rinsate blank should be collected per trip.

9.3.3 A rinsate blank is obtained by pouring analyte-free water over decontaminated sampling equipment. The blank water is collected in the same type of pre-preserved sample vials used for water sample collection. The rinsate blank sample is placed in the sample cooler and treated in the same manner as the other water samples.

9.4 Duplicate and Replicate Split Samples

9.4.1 A duplicate is a sample obtained from the same location at essentially the same time as the true sample. The procedures used to collect both the true sample and the duplicate sample should be identical. An example would be two samples of water taken from a creek, collected directly into the appropriate sample containers from essentially the same location and at essentially the same time.

9.4.2 A replicate split sample is obtained by dividing or splitting one sample into two samples for separate analysis. An example would be collecting a bucket of water from a creek and then pouring that water into two sets of sample containers with each set to be analyzed as a distinct sample.

9.4.3 Either a duplicate or a replicate split sample should be collected for every ten true samples collected at a site. A duplicate water sample is used primarily to assess precision associated with sampling methodology and to a lesser extent sample homogeneity and analytical procedures. A replicate split water sample is collected primarily to assess precision associated with analytical procedures and to a lesser extent sample handling procedures.

9.5 Background

9.5.1 Background samples are collected from locations either on- or off-site where no contamination is expected to exist. Examples of background samples include upgradient monitoring wells and upstream samples.

9.5.2 When sampling contaminated rivers, streams, or other flowing waterways, a background sample should be collected, if possible, from a location upstream from the source of contamination. The background sampling location should be upstream of any potential backwater mixing zone.

10.0 REFERENCES

MDNR Environmental Services Program, MDNR-FSS-001 *Containers, Volumes, Preservatives, Holding Times, and Special Considerations*

MDNR Environmental Services Program, MDNR-FSS-002 *Field Sheet and Chain-of-Custody Record*

MDNR Environmental Services Program, MDNR-FSS-003 *Sample Numbering and Tagging*

MDNR Environmental Services Program, MDNR-FSS-004 *Field Documentation*

MDNR Environmental Services Program, MDNR-FSS-005 *General Sampling Considerations Including the Collection of Grab, Composite, and Modified Composite Samples from Streams and Wastewater Flows*

MDNR Environmental Services Program, MDNR-FSS-007 *Collection of Samples From Wells*

MDNR Environmental Services Program, MDNR-FSS-008 *Collection of Samples From Drums*

MDNR Environmental Services Program, MDNR-FSS-009 *Collection of Samples From Tanks*

MDNR Environmental Services Program, MDNR-FSS-018 *Sample Handling: Field Handling, Transportation, and Delivery to the ESP Lab*

MDNR Environmental Services Program, MDNR-FSS-210 *Quality Assurance/Quality Control for Environmental Data Collection*